Multi-channel on-line chromatographic analysis system for quick air–fuel ratio measurement

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Abstract

Details of the design and construction of a two-channel air–fuel ratio (AFR) chromatograph for the on-line analysis of a single sample of wet combustion gases are given. A thermal conductivity detector (TCD) is used to detect CO_2 and N_2 components, which are separated on a single column system. Then the ratio of the concentration of CO_2 and N_2 is used to determine the AFR in the original sample. The column used is a stainless-steel tube (3 in.$\times 1/8$ in. I.D.) filled with 80 mesh Porapak Q. A switching valve is incorporated to divert the samples between the separating column. The instrument is fully automatic and capable of determining two different AFR measurements in a working time of less than 5 s. It can operate satisfactorily at mixture strengths that are well above stoichiometric levels.

Keywords: Air–fuel ratio; Carbon dioxide; Nitrogen

1. Introduction

The analysis of gases from combustion plants is frequently required for research and control purposes. The mixing pattern of fuel and air can only be described from results of a detailed survey. It is also highly desirable that the equipment used in such a measurement is preferably portable and it is essential that it is fast in operation. Many local air–fuel ratio (AFR) measurements have to be made under different test conditions to understand the detailed AFR distribution within a combustion chamber of a system. As is known, these tests take a long time to perform and they are expensive. Therefore, the use of multi-channel equipment reduces long rig running times and costs [1].

2. Experimental

2.1. Fast air–fuel ratio measurement

The sample processing and analysis methods are briefly outlined, as follows. They consist of a gas chromatographic gas analysis unit capable of analyzing combustion gas mixtures of up to three times the stoichiometric level. The sample is taken isokinetically with a suitable probe and mixed with excess oxygen to ensure that the fuel content of the sample is completely oxidized to carbon dioxide and water in the catalytic furnace. After cooling and dehydration, the sample is quickly passed through the pipelines into the AFR instrument. This consists basically of a thermal conductivity detector (TCD) in which the percentages of CO_2 and N_2 are measured.

After drying, the only remaining gases in the oxygen stream are CO_2, whose concentration is proportional to that of the original fuel content, and N_2, whose concentration is a measure of the original air content. Fast chromatographic separation of the N_2–CO_2 mixture in an oxygen carrier, followed by component detection and peak integration enables a measurement of the N_2 to CO_2 concentration ratio to be made, and then the AFR can be calculated using the following formula:

$$AFR = C \cdot (N_2\% / CO_2\%)$$

In this equation, C is a constant and it is only a function of the composition of fuel and air.

The whole analysis system was designed and constructed by the help of The Rolls Royce (1971) Ltd. A detailed description of the apparatus and system can be found in reference [2]. It has been shown that it is possible to determine the accuracy and repeatability of the instrumentation. With extreme care in the calibration, an accuracy of about ±5% for each AFR measurement can be achieved. For this achievement, first of all it was necessary that the percentage of CO and HC in the combustion products, after the catalytic furnace, be known. Therefore, spot checks on the CO and HC concentrations were made using draeger tubes. Secondly, an attempt was made to obtain a correction factor for the determination of the right AFR of a known HC mixture. For this, a G.P.-grade ethylene and a commercial-grade N_2 mixture was prepared. While these mixtures were passing through the sample process furnace they were diluted with excess oxygen and were completely converted to CO_2 and N_2. Then they were fed into the chromatographic gas analysis unit for the analysis, and hence, the AFR of the known mixture was obtained experimentally. When obtained, the maximum error of these AFR was ±5% and all the other points were also within this error band. It was clearly understood from these investigations that this is the capability of the system with this kind of measurement.

2.2. Chromatographic analysis unit

2.2.1. Sample injection valve

It is essential for fast chromatography, that the samples injected into the chromatographic column should be as small and as discrete as possible. This requires high speed activation. There are two types of valves for sample injection or switching application on the market. In process equipment, either rotary or slide sample valves can be used. An internal volume rotary-type valve usually comes with a fixed volume replacement valve rotor. The sample size in these types of valves is determined by a slot engraved on the valve rotor that can not be altered easily. Here, in this configuration, the more suitable, Servomex pneumatically operated slide valve (Type SV 220) was used. The sample size of these types of valves can simply be determined by drilling the slide with a suitable drill. This seems to be an intrinsic advantage in the slide sample valve usage when compared with the fixed volume rotary type valves. The valve consists of a sliding block unit and a pneumatic chamber. A piston that is sealed with an "O" ring is operated by the diaphragm and it is connected to the slide holder by means of a pin. The positive "push" on and "pull" return action of the slide is controlled by two d.c. solenoid valves. The sample volume of the valve is about 0.05 ml, and this volume of sample is injected directly into the column in the oxygen carrier stream.

2.2.2. Chromatography column

This column is connected directly to the body of the injection valve and consists of a stainless-steel tube (3 in.×1/8 in. I.D.). The column is filled with 80 mesh Porapak Q [3]. The function of the Porapak column is to separate the major components of the gas mixture. With this type of column, coupled to the small volume sample injection valve, a complete separation of the CO_2 and N_2 components can be achieved in a working time of less than 2 s.

2.2.3. Detector

The detector used in this chromatographic system must have a very fast response time and show good sensitivity to CO_2 and N_2 in the oxygen carrier gas. The detector device used is the Servomex micro katharometer (type MK.158) which is a TCD. The TCD, like the FID, is a universal detector responding to most components including oxygen, nitrogen and carbon dioxide. Easy to use with a wide dynamic

range, the TCD allows excellent detection at both high percentage and low ppm concentration ranges. Its response speed and sensitivity are such that it is ideal for use as a detector in gas chromatography, particularly with fine bore packed columns. The TCD consists of reference and measuring chambers, each of which contains two filaments that together form a complete Wheatstone bridge. A constant voltage and constant current must be applied to the bridge in order to exploit the full capabilities of the TCD. A noise-free baseline can be obtained at high sensitivity and the ultimate detection limit of the device is more than adequate to describe. Good absolute accuracy of the system depends upon reliable calibration.

2.2.4. Calibration

The accuracy of the quantitative analysis, of course, depends upon the accuracy of the calibration. Calibration of the two separate chromatograph channels was performed using a set of cylinders filled with gas mixtures of known composition [4]. Then, the relationship between the N_2 peak height and concentration and the CO_2 peak height and concentration was determined. The calibration gases were obtained from the British Oxygen Company (B.O.C.) with certificates of analysis and their compositions are given in Table 1. As can be seen in this table, the calibration for carbon dioxide is taken from 1 to 25% in 5% steps and a typical calibration curve is shown in Fig. 1. At the beginning, both CO_2 and N_2 calibration curves were obtained from the prepared sample cylinder. It was soon realized, however, that the effect of the argon in the air was significant and therefore dry air and oxygen mixtures were used for the nitrogen calibration. The composition of the prepared oxygen and dry air mixtures are given in Table 2. The nitrogen calibration covers the range up to 79% in various percentages. The calibration curves obtained can be seen in Fig. 2. The chromatographic equipment is very sensitive to the N_2, therefore, two calibration curves were obtained from the prepared oxygen and the dry air mixtures, one for each channel, namely channel one and channel two. One important thing must be made clear, the N_2 calibration can be obtained either from the calibration gases or from the dry air and oxygen

Table 1
Calibration gases

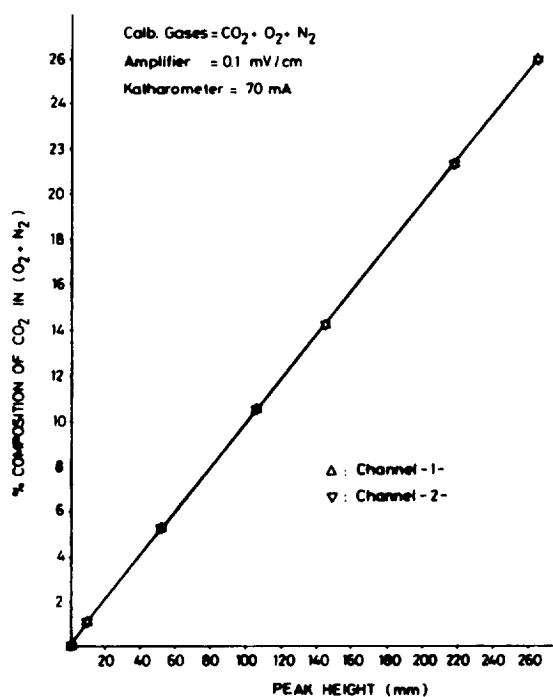| Cylinder number	Mixtures	Analysis (%)	B.O.C.[a] certificate number
	CO_2	1.0	
1	O_2	34.4	5421
	N_2	64.6	
	CO_2	5.2	
2	O_2	39.5	34 485
	N_2	55.3	
	CO_2	10.54	
3	O_2	45.70	34 486
	N_2	43.76	
	CO_2	14.2	
4	O_2	46.5	5613
	N_2	39.3	
	CO_2	21.3	
5	O_2	45.5	34 487
	N_2	33.2	
	CO_2	25.93	
6	O_2	47.60	34 488
	N_2	26.47	

[a]British Oxygen Company

Fig. 1. Calibration for CO_2.

Table 2
Oxygen and air mixtures for N_2 calibration

Cylinder Number	Mixtures	Analysis (%)
1	O_2	84.99
	N_2	15.01
2	O_2	69.98
	N_2	30.02
3	O_2	49.44
	N_2	50.56
4	O_2	29.69
	N_2	70.31
5	O_2	21.0
	N_2	79.0

mixtures. When the same concentrations of N_2 peak heights are compared with each other it can be seen more clearly that the N_2 peak height obtained with the mixture of dry air and oxygen is always higher than the peak height obtained with the calibration gases (Fig. 2). Therefore, one cannot use the calibration curve for N_2 obtained using the calibration gases to determine the correct AFR. If so, this may cause some error that is probably due to the change
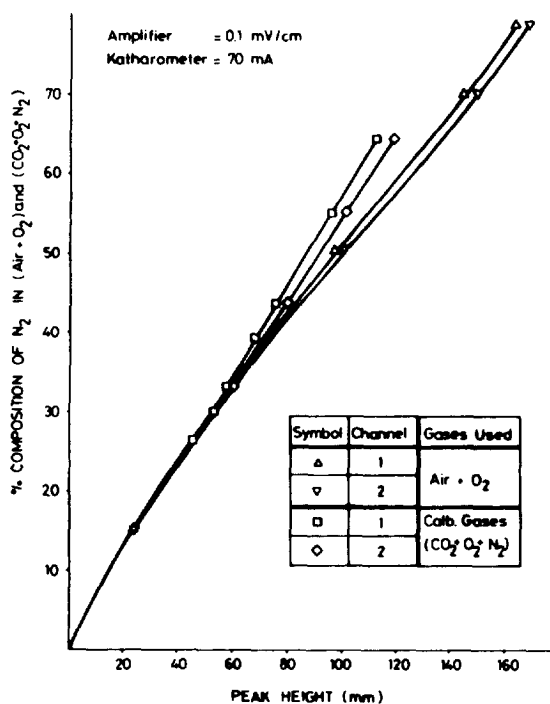

Fig. 2. Calibration for N_2.

in N_2 peak shape. In other words, the N_2 calibration curve must be obtained from the dry air–oxygen mixtures to correspond with actual practice.

When calibration gases were used for the N_2 calibration, the calibration obtained from the calibration gases showed little change in N_2 peak shape with increasing CO_2 concentration. The chromatogram peak appeared as a "W" shape when the concentration of CO_2 in the calibration gases was above 5%, as shown in Fig. 3. This continued with increasing CO_2 concentrations. When the dry air–oxygen mixtures were used for the N_2 calibration, the "W"-shaped peaks never appeared. It was understood from these investigations that high CO_2 concentrations were causing this effect.

As described previously, the calibration curves are plotted as percentages of CO_2 and N_2 against peak heights, assuming that the geometrical shapes of the peaks are always identical. In the preceding paragraph it was shown that the geometrical shapes of the peaks change slightly with the concentration of both constituents. This may, therefore, introduce some error into the calibration. However, more accurate calibrations of concentration against trace area could be obtained using an integrator unit.

3. Conclusion

The two-channel AFR unit described enables measurements to be made in working times of less than 5 s. Calibration of the instrument before and after experimental testing is important if reliable results are to be obtained. The best and quickest procedure is to use a set of cylinders filled with gas mixtures of known composition for the CO_2 calibration and to use dry air and oxygen mixtures for the N_2 calibration. Thus, with extreme care in the calibration, an accuracy of about ±5% for each AFR measurement can be achieved, but in the first applications of the instrument to the experimental work, the accuracy of the system was about ±8%. Therefore, the absolute accuracy of the system needs to be improved. Using an integrator for the chromatogram peaks can be a first step in improving this process. Secondly, when the analyst selects the right configuration of the instrumentation and knows suitable methods for handling different kinds of samples,
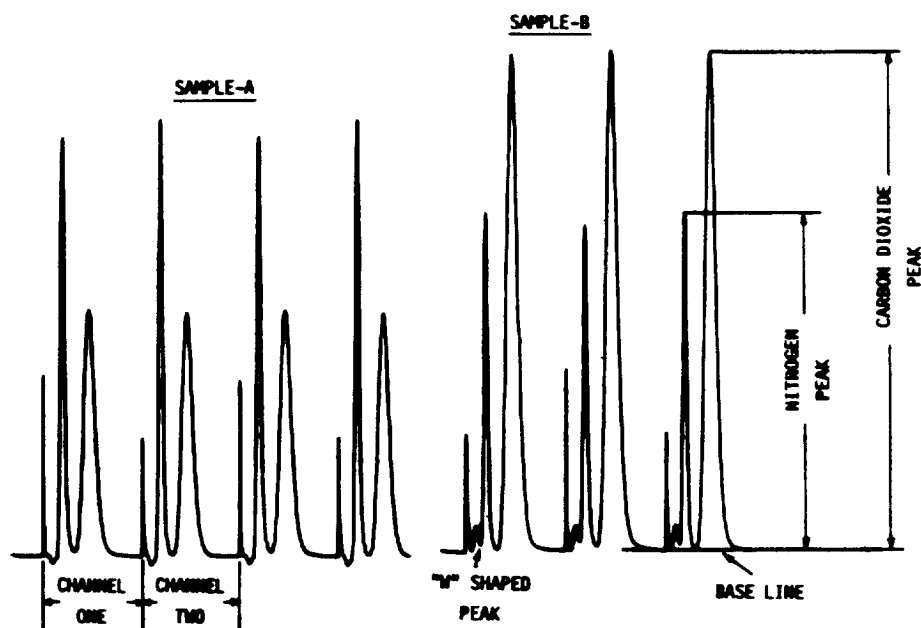
Fig. 3. Chromatogram of the N_2 and CO_2.

depending on the objectives of the analysis, an expected or much higher performance can be achieved in gas chromatography. Finally, as Karrer [5] said in 1947, not only the chemist, but every scientist must also benefit from chromatography for quick analysis.

Acknowledgments

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